

# Online Research @ Cardiff

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository: <https://orca.cardiff.ac.uk/id/eprint/94470/>

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Mishra, Abhishek Kumar, Roldan Martinez, Alberto ORCID:  
<https://orcid.org/0000-0003-0353-9004> and De Leeuw, Nora ORCID:  
<https://orcid.org/0000-0002-8271-0545> 2016. A density functional theory study of the adsorption behaviour of CO<sub>2</sub> on Cu<sub>2</sub>O surfaces. Journal of Chemical Physics 145 (4) , 044709. 10.1063/1.4958804 file

Publishers page: <http://dx.doi.org/10.1063/1.4958804>  
<<http://dx.doi.org/10.1063/1.4958804>>

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies.

See

<http://orca.cf.ac.uk/policies.html> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



## A density functional theory study of the adsorption behaviour of CO<sub>2</sub> on Cu<sub>2</sub>O surfaces

Abhishek Kumar Mishra, Alberto Roldan, and Nora H. de Leeuw

Citation: *The Journal of Chemical Physics* **145**, 044709 (2016); doi: 10.1063/1.4958804

View online: <http://dx.doi.org/10.1063/1.4958804>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/145/4?ver=pdfcov>

Published by the AIP Publishing

### Articles you may be interested in

CO<sub>2</sub> adsorption on TiO<sub>2</sub>(101) anatase: A dispersion-corrected density functional theory study

J. Chem. Phys. **135**, 124701 (2011); 10.1063/1.3638181

Structure and activity relationship for CO and O<sub>2</sub> adsorption over gold nanoparticles using density functional theory and artificial neural networks

J. Chem. Phys. **132**, 174113 (2010); 10.1063/1.3369007

Coadsorption of CO and NO on the Cu<sub>2</sub>O (111) surface: A periodic density functional theory study

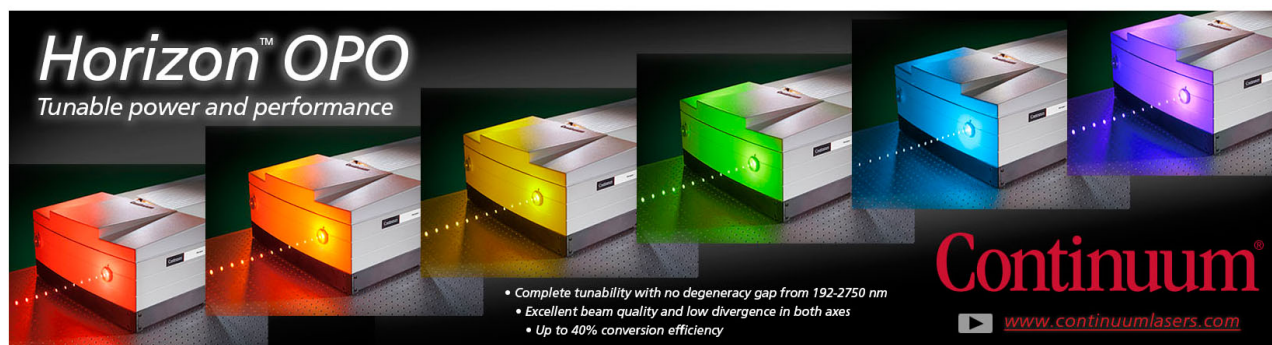
J. Chem. Phys. **131**, 174503 (2009); 10.1063/1.3251055

The adsorption of CO on charged and neutral Au and Au<sub>2</sub>: A comparison between wave-function based and density functional theory

J. Chem. Phys. **128**, 124302 (2008); 10.1063/1.2834693

Density functional theory study of C<sub>x</sub>H<sub>x</sub> (x = 1 – 3) adsorption on clean and CO precovered Rh(111) surfaces

J. Chem. Phys. **127**, 024705 (2007); 10.1063/1.2751155



**Horizon™ OPO**  
Tunable power and performance

Complete tunability with no degeneracy gap from 192-2750 nm  
Excellent beam quality and low divergence in both axes  
Up to 40% conversion efficiency

**Continuum®**  
[www.continuumlasers.com](http://www.continuumlasers.com)

# A density functional theory study of the adsorption behaviour of CO<sub>2</sub> on Cu<sub>2</sub>O surfaces

Abhishek Kumar Mishra,<sup>1,2,a)</sup> Alberto Roldan,<sup>3</sup> and Nora H. de Leeuw<sup>2,3,a)</sup>

<sup>1</sup>Research & Development, University of Petroleum and Energy Studies (UPES), Bidholi, Dehradun 248007, India

<sup>2</sup>Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

<sup>3</sup>School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

(Received 13 May 2016; accepted 1 July 2016; published online 29 July 2016)

Copper has many applications, particularly in electro-catalysis, where the oxidation state of the copper electrode plays a significant role in the selectivity towards products. Although copper-based materials have clear potential as catalysts in the reduction of CO<sub>2</sub> and conversion to products, fundamental understanding of CO<sub>2</sub> adsorption and activation on different copper oxide surfaces is still limited. We have used DFT+U methodology to study the surface reconstruction of the three most exposed (111), (110), and (001) surfaces of Cu<sub>2</sub>O with different possible terminations. Considering several adsorbate geometries, we have investigated CO<sub>2</sub> adsorption on five different possible terminations and proposed eight different configurations in which CO<sub>2</sub> binds with the surface. Similar to earlier findings, CO<sub>2</sub> binds weakly with the most stable Cu<sub>2</sub>O(111):O surface showing no molecular activation, whereas a number of other surfaces, which can appear in the Cu<sub>2</sub>O particles morphology, show stronger binding as well as activation of the CO<sub>2</sub> molecule. Different CO<sub>2</sub> coverages were studied and a detailed structural and electronic charge analysis is presented. The activation of the CO<sub>2</sub> molecule is characterized by structural transformations and charge transfer between the surface and the CO<sub>2</sub> molecule, which is further confirmed by considerable red shifts in the vibrational frequencies. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4958804>]

## I. INTRODUCTION

Copper is a unique metal owing to its ability to selectively produce hydrocarbons through the electro-reduction of CO<sub>2</sub>,<sup>1,2</sup> where the oxidation state of the Cu electrode plays an important role in the product selectivity. The direct reduction of CO<sub>2</sub> to methanol (CH<sub>3</sub>OH) is known to occur on oxidized Cu electrodes, which show an increase in the methanol formation by an order of magnitude compared to metallic copper.<sup>3</sup> The surface structure of oxidized copper resembles the Cu<sub>2</sub>O (111)<sup>4,5</sup> surface and it reduces CO<sub>2</sub> to CH<sub>3</sub>OH at rates remarkably higher than either air-oxidized or anodized Cu.<sup>5</sup> In addition, our recent density functional theory (DFT) based calculations of CO<sub>2</sub> hydrogenation on the most stable (111) surface of Cu<sub>2</sub>O show that it is a suitable catalyst for CO<sub>2</sub> conversion to formate and formic acid under mild conditions.<sup>6</sup> Surface analysis of these oxides, before and after the reaction, shows mixed oxidation states (Cu<sub>2</sub>O, Cu<sub>4</sub>O<sub>3</sub>, and CuO) depending on the method of preparation.<sup>7</sup> Recently, it has been demonstrated that CuO–Cu<sub>2</sub>O nanorod arrays prepared on Cu substrates can drive the efficient solar photo-conversion of CO<sub>2</sub> to methanol.<sup>8</sup>

The catalytic process is affected considerably by the catalyst structure, with different shapes and surface arrange-

ments having a large impact on the catalyst's activity and stability. Furthermore, surface structures and crystallographic facets of metal oxides have been found to control the gas sensing properties of metal oxide-based sensors.<sup>9–11</sup> By controlling the size and morphology, one can fine tune the strength of surface adsorption and reactivity to meet the stringent selectivity and activity requirements in a catalytic process. For example, our recent investigations of CO<sub>2</sub> activation on a number of Cu(II) oxide surfaces revealed that surface structures have significant effects on CO<sub>2</sub> activation and binding energies.<sup>12</sup>

The most exposed surfaces of Cu<sub>2</sub>O are the (111), (110), and (001),<sup>13</sup> with the (111) surface the most stable and most studied among these surfaces.<sup>14–19</sup> However, shape-controlled synthesis of Cu<sub>2</sub>O crystals has been investigated widely and a variety of morphologies has been synthesised successfully.<sup>20–25</sup> Recently, a study by Sun *et al.* on the crystal facet-dependent effect of polyhedral Cu<sub>2</sub>O micro-crystals, that exposed different Miller index facets, showed that the catalytic performance can be enhanced by high-index facets,<sup>26</sup> Furthermore, copper(I) oxide nano clusters have been studied recently to understand the methanol formation through DFT based calculations.<sup>27</sup>

The adsorption of molecules on a catalyst surface is the first step in their activation and conversion in any catalytic process. CO<sub>2</sub> adsorption on the Cu<sub>2</sub>O(111) surface has been investigated by Wu *et al.*,<sup>18,19</sup> and Bendavid and Carter,<sup>28</sup> using

<sup>a)</sup>Electronic addresses: [akmishra@ddn.upes.ac.in](mailto:akmishra@ddn.upes.ac.in), [abhishek.mishra@ucl.ac.uk](mailto:abhishek.mishra@ucl.ac.uk), and [deleeuw@cardiff.ac.uk](mailto:deleeuw@cardiff.ac.uk)





DFT calculations. Wu *et al.*,<sup>19</sup> investigated CO<sub>2</sub> adsorption on the Cu<sub>2</sub>O(111) surface, using the standard generalized gradient approximation (GGA) and identified that CO<sub>2</sub> binds as a linear molecule in a tilted configuration to the surface, with its oxygen atom coordinated to a coordinatively unsaturated surface copper atom, releasing an adsorption energy of 26.8 kJ/mol. However, it is now well known that pure GGA can lead to considerable errors when calculating reactions where 3d-metal oxides are oxidized by means other than by oxygen. Reaction energies for these processes become more accurate when the so-called DFT+U method is applied.<sup>29</sup> Bendavid and Carter<sup>28</sup> recently investigated CO<sub>2</sub> adsorption on the Cu<sub>2</sub>O(111) using the DFT+U method and showed via comparison to adsorption energies derived by standard DFT that the U parameter is necessary. Their choice of U = 6 eV was based on their earlier work,<sup>30</sup> where they determined and compared different values of U to earlier DFT+U studies on Cu<sub>2</sub>O and CuO.<sup>31–33</sup> The selection of their U value was based solely on its accuracy to predict the equilibrium lattice constant for Cu<sub>2</sub>O. However, experimentally it is found that copper oxide surfaces consist of mixed Cu<sub>2</sub>O and CuO surface species, whereas molecule interactions can also alter the oxidation state of the copper oxide surface, i.e., through –OH groups.<sup>30</sup> Therefore, we recently determined a single U parameter to describe adequately both Cu<sub>2</sub>O and CuO in terms of experimental properties.<sup>12</sup> In the present work, we have employed DFT with this Hubbard U correction to explore CO<sub>2</sub> adsorption on different non-polar stoichiometric terminations of the (111), (110), and (001) surfaces of Cu<sub>2</sub>O. We first describe the reconstruction of the different surfaces and their electronic properties, followed by a detailed discussion of the CO<sub>2</sub> adsorption behaviour.

## II. COMPUTATIONAL DETAILS

All the calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) with plane-wave basis set.<sup>34–37</sup> We have employed plane-wave DFT+U<sup>38</sup> with the PBE<sup>39,40</sup> exchange-correlation functional and the formalism of Dudarev *et al.*<sup>38</sup> The different Cu<sub>2</sub>O surfaces were obtained by the METADISE code,<sup>41</sup> providing different non-polar surface terminations.<sup>42</sup> At the base of the surface simulation cell, two layers of atoms were fixed at their optimised bulk positions to simulate the bulk phase of the Cu<sub>2</sub>O. Above these two layers, the surface is represented by three layers of atoms, whose positions are allowed to change freely during optimization. In each case, the vacuum region above the surface was 12 Å, i.e., large enough to avoid interactions between the periodic slabs. We sampled (1 × 1) and (2 × 2) supercells with 5 × 5 × 1 and 3 × 3 × 1 Monkhorst and Pack<sup>43</sup> k-point mesh, respectively. Such dense grids and a truncation kinetic energy of 450 eV for the plane waves ensured an accurate description of properties that are influenced by sharp features in the density of states. A total convergence better than 10<sup>–5</sup> was reached and the interatomic forces were minimized to 0.01 eV/Å for structural relaxation calculations.

The surface energies of the relaxed slabs were obtained using a combination of calculations for the relaxed and unrelaxed surfaces. After surface relaxation, the top and

bottom surfaces are not equivalent and therefore we also need to consider the unrelaxed surface energy ( $\gamma_u$ ) in order to calculate the final surface energy of the relaxed surface. The unrelaxed surface energy is the surface energy before any surface optimisation and is calculated as

$$\gamma_u = \frac{E_{slab,u} - nE_{bulk}}{2A}, \quad (1)$$

where  $E_{slab,u}$  is the energy of the unrelaxed slab,  $nE_{bulk}$  is the energy of an equal number of bulk atoms, and  $A$  is the surface area of one side of the slab. Using this value, it is then possible to calculate the relaxed surface energy ( $\gamma_r$ ) from the total energy of the relaxed slab.

The relaxed surface energy,  $\gamma_r$ , is given by

$$\gamma_r = \frac{E_{slab,r} - nE_{bulk}}{A} - \gamma_u, \quad (2)$$

where  $E_{slab,r}$  is the energy of the relaxed slab.

The equilibrium morphology of a Cu<sub>2</sub>O particle (ignoring higher Miller indices) was constructed using Wulff's method,<sup>44</sup> which requires that the distance to a given surface from the center of the particle is proportional to the surface energy.

While modelling the CO<sub>2</sub> molecule, we have also used the implementation of the DFT-D2 approach described by Grimme<sup>45</sup> to account for long-range dispersion forces. The isolated molecule was modelled in the centre of a big cell with broken symmetry and lattice constants of 20 Å, sampling only the gamma-point of the Brillouin zone with the same accuracy parameters described for the surfaces.

The adsorption energy per molecule was calculated from the relation

$$E_{ads} = E_{surf+mol} - (E_{surf} + E_{mol}), \quad (3)$$

where  $E_{surf+mol}$  is the total energy of the adsorbate-substrate system,  $E_{surf}$  is the energy of the naked surface slab, and  $E_{mol}$  is the energy of the isolated CO<sub>2</sub> molecule. Within this definition, a negative adsorption energy indicates an exothermic process.

## III. RESULT AND DISCUSSION

In a recent work, we found that a value of  $U_{eff} = 7$  eV results in the accurate reproduction of the structural parameters of Cu<sub>2</sub>O and a proper description of the Cu(II) oxide.<sup>12</sup> At this  $U_{eff}$  value, we found the lattice parameter of Cu<sub>2</sub>O to be 4.270 Å, which is very close to the experimental value of 4.2696 Å.<sup>46</sup> Other structural parameters were also found to be in close agreement with the experimental values.<sup>46</sup> We have therefore modelled the different Cu<sub>2</sub>O surfaces using the same  $U_{eff}$  value and employing the same bulk structural parameters.<sup>12</sup>

### A. Surface reconstructions

In this section (Sec. III A), we have described in detail the reconstruction of the different terminations of three low-index Cu<sub>2</sub>O surfaces: (111), (110), and (001). We

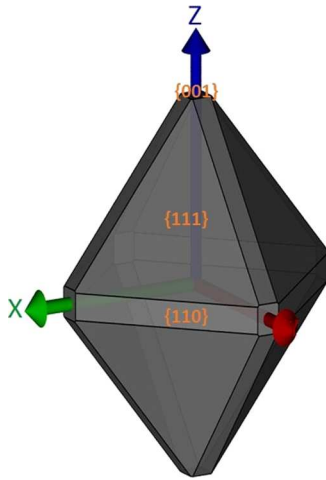


FIG. 1. The Wulff morphology of  $\text{Cu}_2\text{O}$  particle determined from calculated surface energies.

have calculated the surface energies of the different surface terminations from Equation (2) and determined the Wulff morphology<sup>44</sup> of the  $\text{Cu}_2\text{O}$  crystal, as shown in Fig. 1. The calculated surface energies ( $\gamma_r$ ), the work functions, and the electronic band gaps of the different surfaces are listed in Table I.

### 1. $\text{Cu}_2\text{O}(111)$ surface

*a. (111):O.* In agreement with Soon *et al.*,<sup>47</sup> we found that the most stable surface is the stoichiometric non-polar oxygen-terminated (111) surface, (111):O, with a surface energy of  $1.08 \text{ J/m}^2$ . The work function calculated with DFT+U is  $4.98 \text{ eV}$ , which is close to the experimental range of  $4.62\text{--}4.84 \text{ eV}$ .<sup>48</sup> This surface consists of four distinct types of atoms: unsaturated (singly coordinated) surface copper atoms  $\text{Cu}_{\text{CUS}}$ , outermost surface oxygens  $\text{O}_{\text{SUF}}$ , saturated copper atoms with linear O–Cu–O bond symmetry  $\text{Cu}_{\text{CSA}}$ , and sub-surface oxygens that are 4-fold coordinated  $\text{O}_{\text{SUB}}$  (Fig. 2). The unsaturated copper atoms ( $\text{Cu}_{\text{CUS}}$ ) act as Lewis acid sites, where most of the surface reactions are believed to take place.<sup>49</sup>

After relaxation, the distance of the  $\text{Cu}_{\text{CSA}}$  atoms to  $\text{O}_{\text{SUF}}$  atoms decreases from  $1.85$  to  $1.82 \text{ \AA}$ , but increases to the  $\text{O}_{\text{SUB}}$  atom to  $1.86 \text{ \AA}$ . As a result, these  $\text{Cu}_{\text{CSA}}$  atoms become more exposed. The top  $\text{Cu}_{\text{CUS}}$  atoms also move outwards so that the vertical bond length between  $\text{Cu}_{\text{CUS}}$  and the topmost O atoms found in the second trilayer increases from  $1.85$  to  $1.91 \text{ \AA}$ ,

TABLE I. The calculated relaxed surface energies ( $\gamma_r$ ), work functions ( $\phi$ ), and the bandgaps ( $E_g$ ) of different  $\text{Cu}_2\text{O}$  surfaces.

Surface	$\gamma_r \text{ (J/m}^2\text{)}$	$\phi \text{ (eV)}$	$E_g \text{ (eV)}$
(111):O	1.08	4.98	0.78
(111):Cu	1.92	5.10	...
(110):Cu	1.24	5.41	0.30
(110):Cu–O	1.54	4.39	0.15
(100):Cu	1.62	4.54	...

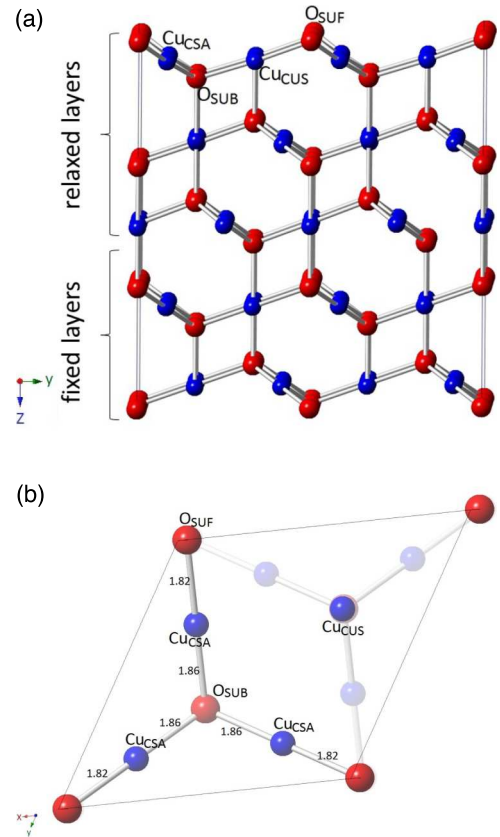


FIG. 2. The  $\text{Cu}_2\text{O}(111):\text{O}$  terminated relaxed surface side view (a) and top view (b). We have shown a  $(2 \times 2)$  cell in side view with periodic images of atoms for clearer visualization of bonding in all surface figures. Blue and red balls indicate Cu and O atoms, respectively, in all figures. The bond length values are in  $\text{\AA}$ .

while the vertical bond length from the sub-surface oxygen atoms to the copper atoms in the second layer also increases to  $1.89 \text{ \AA}$ . We investigated the electronic density of states (DOS) (Fig. 3(a)) of this surface and found that the bandgap slightly decreases by  $0.78 \text{ eV}$  from the calculated value of  $0.89 \text{ eV}$  for the bulk  $\text{Cu}_2\text{O}$  material. The calculated values of the bandgap are expected to be under-estimated as DFT+U fails in the accurate prediction of bandgaps for  $\text{Cu}_2\text{O}$ .<sup>12,32</sup> The calculated projected DOS shows that both valence band maxima (VBM) and conduction band minima (CBM) mainly consist of O ( $2p$ ) and Cu ( $3d$ ) orbitals, respectively, while contributions from other orbitals are much less.

*b. (111):Cu.* We reconstructed another non-polar stoichiometric (111) surface with a Cu termination ((111):Cu), which, however, is found to be less stable by  $0.84 \text{ J/m}^2$  than the (111):O surface. The work function is found to increase slightly to  $5.10 \text{ eV}$ . The presence of two Cu atoms at both top and bottom of the slab makes the (111):Cu surface non-polar, while maintaining the bulk  $\text{Cu}_2\text{O}$  ratio of Cu and O atoms (an unrelaxed  $(2 \times 2)$  supercell is shown in Fig. S1 of the [supplementary material](#)). After relaxation, we noted significant changes in the positions of the top copper atoms, which moved down below the level of the O atoms. As a result, the O atoms in the relaxed surface are more exposed than the Cu atoms (Fig. 4). The Cu–O bond distance to these two Cu atoms increases slightly by  $0.01 \text{ \AA}$ , while the vertical bond

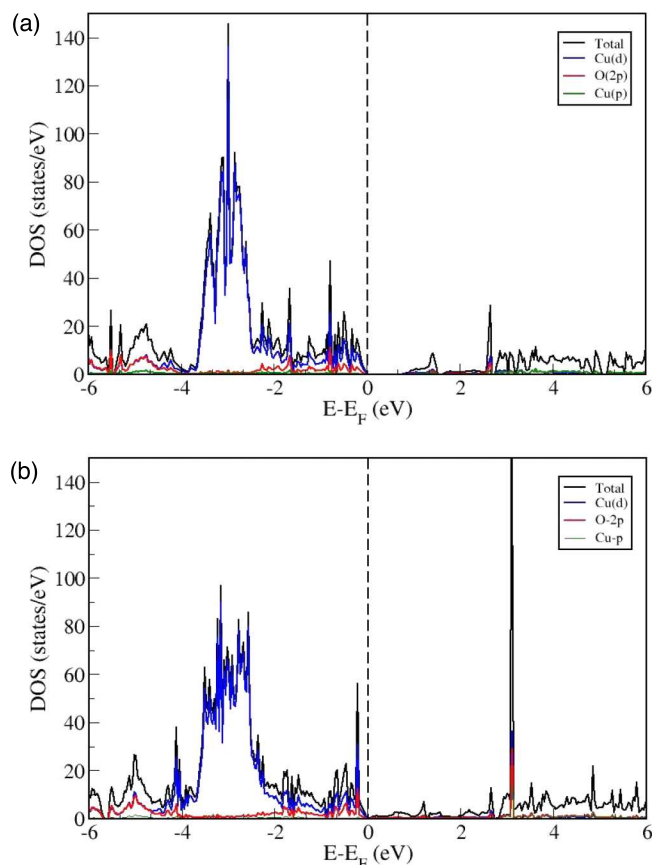


FIG. 3. Electronic DOS of  $\text{Cu}_2\text{O}$  (a) (111):O and (b) (111):Cu terminated surfaces with Fermi-level set to zero.

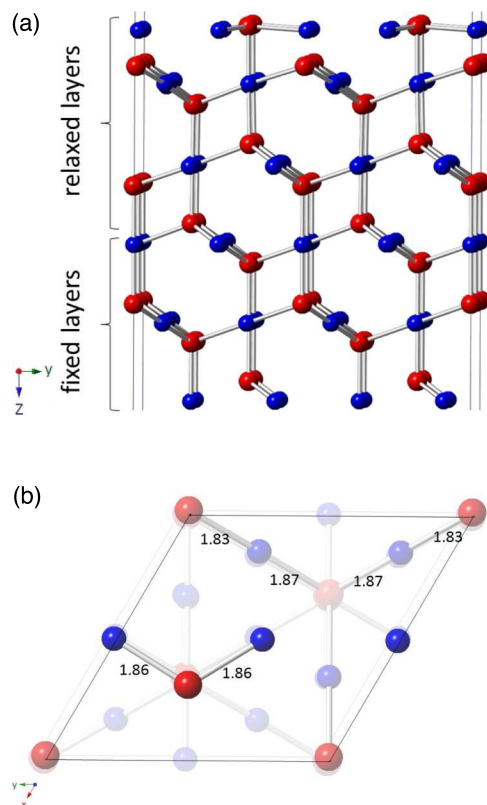


FIG. 4. The  $\text{Cu}_2\text{O}(111):\text{Cu}$  terminated relaxed surface side (a) and top view (b). The bond length values are in Å.

distance to the top O atoms from Cu atoms in the second layer decreases slightly by 0.01 Å. Other Cu–O bond distances in the second and third layers remain unchanged. We observed a finite number of states near the Fermi level in the electronic DOS of this surface and hence propose that this surface is conducting (Fig. 3(b)).

## 2. $\text{Cu}_2\text{O}(110)$ surface

*a. (110):Cu.* This surface consists of Cu atoms at the top of the first layer (Fig. S2 of the [supplementary material](#)) and hence we labelled this termination as (110):Cu. This is the second most stable surface with a surface energy of 1.24 J/m<sup>2</sup>, while the work function is further increased to 5.41 eV. The top Cu atoms are connected to the 4-coordinated oxygen atoms (marked  $\text{O}_A$ ), which are connected tetrahedrally to three more Cu atoms. The other type of O atoms (marked  $\text{O}_B$ ) are 3-coordinated to copper atoms. After relaxation, these top copper atoms bend along the x-axis thereby increasing their distance to  $\text{O}_A$  atoms from 1.85 to 1.90 Å (Fig. 5). During the surface relaxation, the  $\text{O}_A$  atoms moved up, increasing the distance from the Cu atoms of the second layer from 1.85 to 1.91 Å. The  $\text{O}_B$  oxygens also move so that their distance to the lower Cu atoms changes to 1.84 from 1.85 Å. The bond length changes in the second layer are about 0.02 Å, while in the third layer they are less than 0.01 Å.

*b. (110):Cu–O.* In this termination, the surface consists of both Cu and O atoms at the top (labelled (110):Cu–O) and

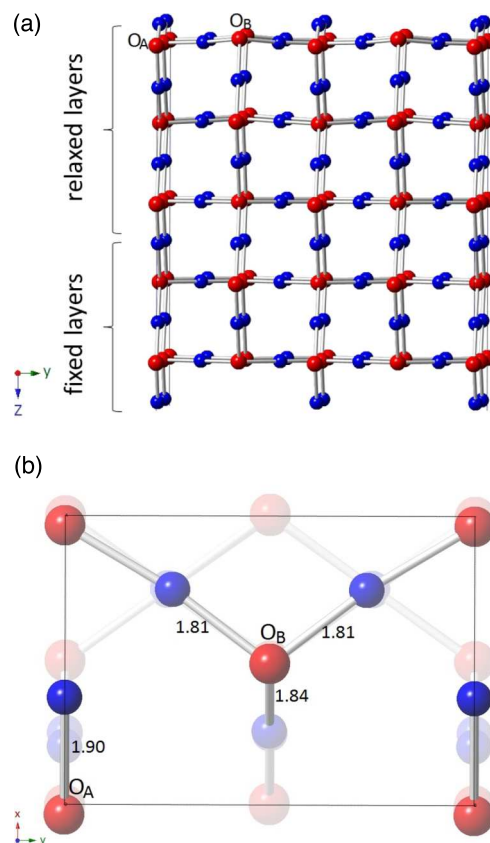


FIG. 5. The  $\text{Cu}_2\text{O}(110):\text{Cu}$  terminated relaxed surface side (a) and top view (b). The bond length values are in Å.

the calculated surface energy is  $1.54 \text{ J/m}^2$ . The work function is found to be the lowest of the surfaces considered at  $4.39 \text{ eV}$ . During the reconstruction to remove the surface dipole, while keeping the ratio of Cu and O atoms the same as in the bulk, the oxygen atoms are rearranged at the top and bottom of the surface (Fig. S3 of the [supplementary material](#)). There are two distinct types of copper atoms below the top Cu–O layer, marked  $\text{Cu}_A$  and  $\text{Cu}_B$ . The  $\text{Cu}_A$  atoms are doubly coordinated to oxygens in the top and second layers, while the  $\text{Cu}_B$  atoms are only singly coordinated to an oxygen atom in the second layer. After relaxation, the top Cu and O atoms are closer and create weak Cu–O bonds of  $2.10$  and  $2.18 \text{ \AA}$  in length (Fig. 6). The  $\text{Cu}_B$  type atoms are also rearranged and, after relaxation, these atoms connect with top O atoms ( $d_{\text{Cu}_B\text{--O}} = 1.87 \text{ \AA}$ ).

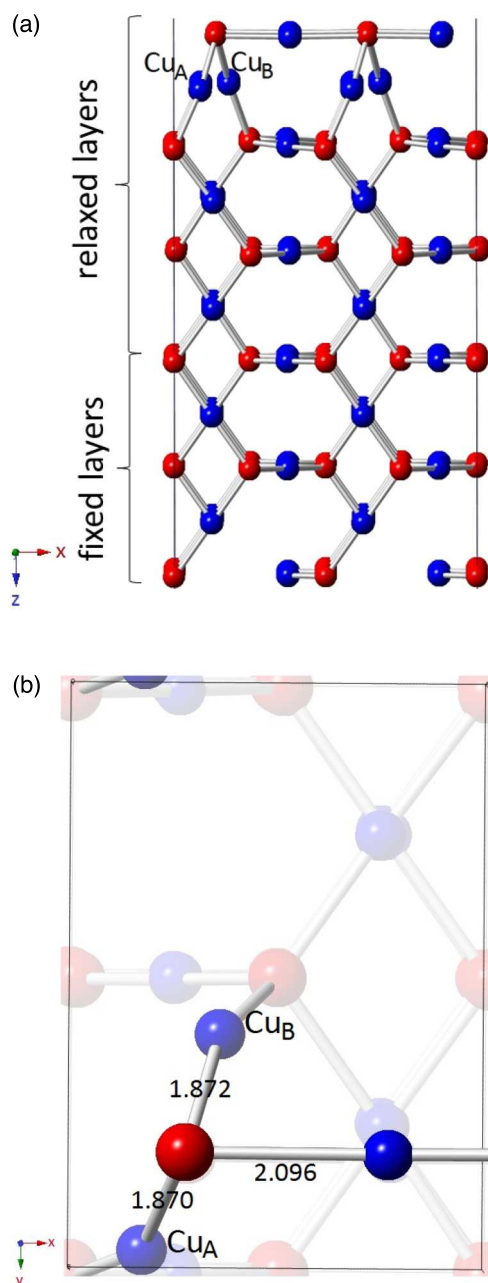


FIG. 6. The  $\text{Cu}_2\text{O}(110)\text{:Cu-O}$  terminated relaxed surface side (a) and top view (b). The bond length values are in  $\text{\AA}$ .

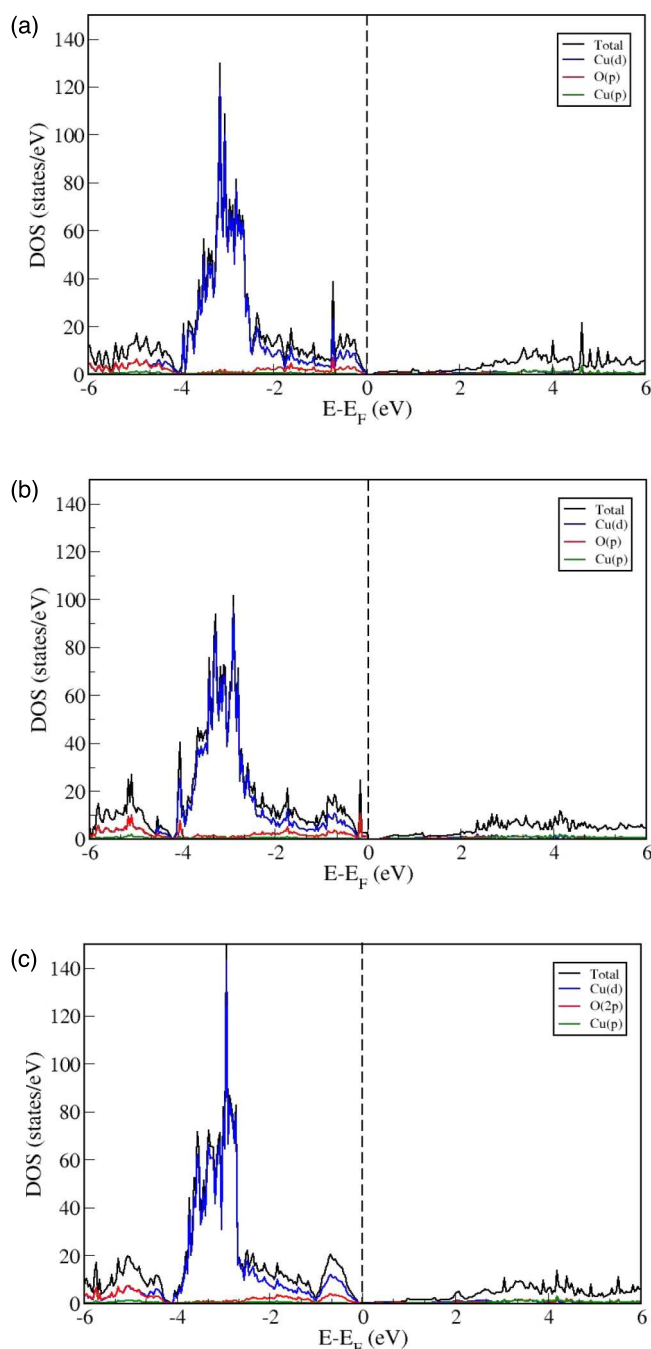


FIG. 7. Electronic DOS of  $\text{Cu}_2\text{O}$  (a)  $(110)\text{:Cu}$ , (b)  $(110)\text{:Cu-O}$ , and (c)  $(001)\text{:Cu}$  terminated surfaces with Fermi-level set to zero.

The Cu–O bond distances in the second tri-layer increase up to  $1.89 \text{ \AA}$ , while there are no structural changes in the third tri-layer.

We calculated the electronic DOS for both terminations and found that the bandgaps for the  $(110)$  surfaces are quite low, at  $0.30$  and  $0.15 \text{ eV}$  for the  $(110)\text{:Cu}$  and  $(110)\text{:Cu-O}$  terminations, respectively (Fig. 7).

### 3. $\text{Cu}_2\text{O}(001)$ surface

*a.  $(001)\text{:Cu}$ .* The  $(001)\text{:Cu}$  is the only non-polar stoichiometric termination of the  $(001)$  surface. Its surface



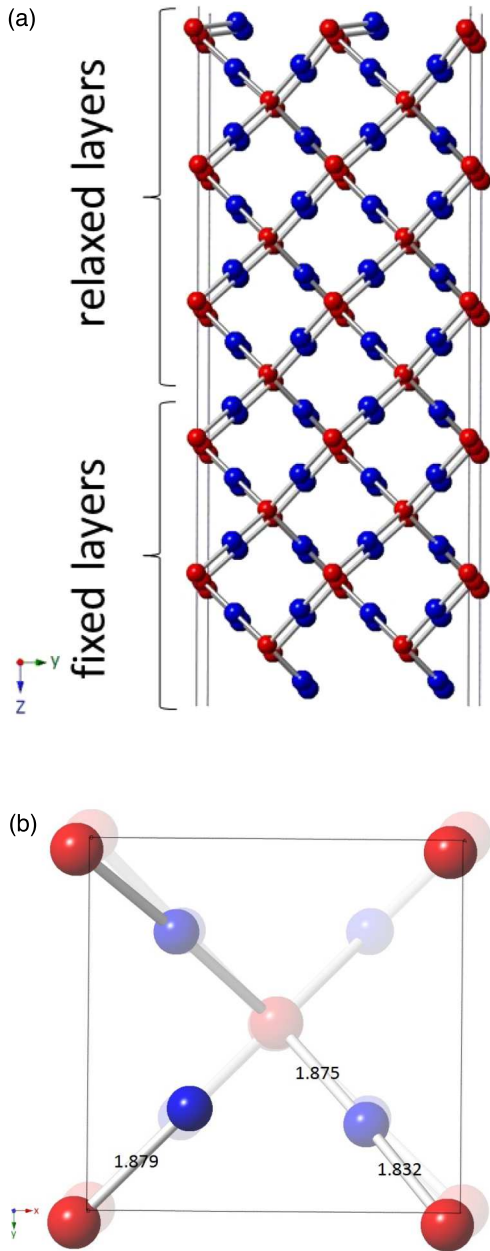


FIG. 8. The  $\text{Cu}_2\text{O}(001):\text{Cu}$  terminated relaxed surface side (a) and top view (b). The bond length values are in Å.

energy is calculated at  $1.62 \text{ J/m}^2$ , which is  $0.46 \text{ J/m}^2$  larger than the surface energy of the most stable  $\text{Cu}_2\text{O}(111):\text{O}$  surface, while the work function is  $4.54 \text{ eV}$ . This surface consists of Cu atoms in the top layer connected to oxygen atoms below, which in turn are connected to two copper atoms in the layer below (Fig. S4 of the [supplementary material](#)). We noted that after relaxation, the top Cu atoms moved down and became less exposed and the Cu–O bond distance increased from  $1.85$  to  $1.88 \text{ Å}$  (Fig. 8). Cu atoms in the second layer move up to shorten the bond length to oxygen atoms in the top layer from  $1.85$  to  $1.83 \text{ Å}$ . We also noted that the Cu–O bond distance in all other relaxed surfaces increases from  $1.85 \text{ Å}$  and varies from  $1.86$  to  $1.88 \text{ Å}$ . With finite states near the Fermi level, this surface is also found to be conducting (Fig. 7).

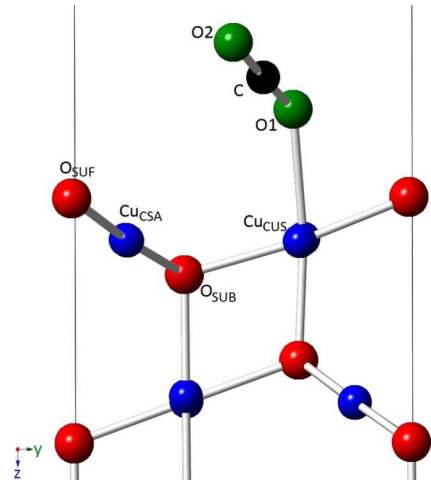


FIG. 9. The  $\text{CO}_2$  molecule adsorbed on the  $\text{Cu}_2\text{O}(111):\text{O}$  terminated surface. Black balls indicate C atom of  $\text{CO}_2$  molecule, green balls indicate O atoms of the molecule, while blue and red balls denote the surface Cu and O atoms in all the figures.

## B. $\text{CO}_2$ adsorption

### 1. $\text{Cu}_2\text{O}(111)$ surface

*a. (111):O surface.* A  $(1 \times 1)$  slab ( $a = b = 6.04 \text{ Å}$ ) consists of 20 copper and 10 oxygen atoms. We first considered the  $(1 \times 1)$  cell of the (111) surface for  $\text{CO}_2$  adsorption and investigated a number of initial configurations with different orientations of the  $\text{CO}_2$  molecule. We found that the  $\text{CO}_2$  molecule moved away from the (111):O surface for all configurations, except where we placed it near the coordinatively unsaturated surface copper,  $\text{Cu}_{\text{CUS}}$ . In this configuration one of the oxygen atoms, O1, of the  $\text{CO}_2$  molecule binds weakly with this  $\text{Cu}_{\text{CUS}}$  copper atom, as shown in Fig. 9. The  $\text{CO}_2$  molecule remains almost linear with an angle of  $176.9^\circ$ . The distance between the oxygen atom O1 of the  $\text{CO}_2$  molecule and  $\text{Cu}_{\text{CUS}}$  is found to be  $2.05 \text{ Å}$ , and the C–O bond between C and this O1 atom is slightly stretched at  $1.19 \text{ Å}$ , while the C–O2 bond length is found to be around  $1.17 \text{ Å}$ . Cu–O bond lengths in the slab also change slightly as a result of  $\text{CO}_2$  adsorption, where the vertical bond distance between  $\text{Cu}_{\text{CUS}}$  (coordinated to the O1 atom of the  $\text{CO}_2$  molecule) and the topmost O atom found in the second trilayer shortens from  $1.91$  to  $1.88 \text{ Å}$ . The adsorption energy in this configuration is  $-51.0 \text{ kJ/mol}$ .

In order to assess the effect of  $\text{CO}_2$  coverage, we repeated our calculation by placing one  $\text{CO}_2$  molecule in a  $(2 \times 2)$  supercell; we found that the adsorption energy increases to  $-56.1 \text{ kJ/mol}$ , but with negligible changes in the  $\text{CO}_2$  geometry. Adsorption geometries of the  $\text{CO}_2$  molecule on

TABLE II. The adsorption energies and the characteristic parameter values of the  $\text{CO}_2$  adsorbed geometry in the  $(1 \times 1)$  and the  $(2 \times 2)$  supercell of the  $\text{Cu}_2\text{O}(111):\text{O}$  surface.

Supercell	$E_{\text{ads}}$ (kJ/mol)	$\angle \text{CO}_2$ (deg)	$d_{\text{C-O1}}$ (Å)	$d_{\text{C-O2}}$ (Å)	$d_{\text{O1-Cu}_{\text{CUS}}}$ (Å)
$(1 \times 1)$	-51.0	176.9	1.19	1.17	2.05
$(2 \times 2)$	-56.1	178.3	1.18	1.18	2.05



TABLE III. Vibrational frequencies ( $\text{cm}^{-1}$ ) and Bader charges ( $e^-$ ) comparison of the atoms in the adsorbed  $\text{CO}_2$  molecule and the  $\text{Cu}_2\text{O}(111):\text{O}$  surface atoms bonded with the molecule to that of the atoms in the isolated  $\text{CO}_2$  molecule and the bare surface in the  $(1 \times 1)$  cell.

Atoms and vibrational modes	C	O1	O2	$\text{Cu}_{\text{CUS}}$	$\nu_{\text{as}}$	$\nu_{\text{s}}$	$\nu_{\text{b}}$
Adsorbed $\text{CO}_2$ molecule	2.08	-1.07	-1.02	0.50	2332	1292	567
Isolated $\text{CO}_2$ molecule	2.08	-1.04	-1.04	...	2355	1316	632
Bare surface	...	...	...	0.44	...	...	...

both  $(1 \times 1)$  and  $(2 \times 2)$  supercell are given in Table II. Our calculated geometrical parameters of the adsorbed  $\text{CO}_2$  molecule and the binding energies are in reasonable agreement with the recent work of Bendavid *et al.*, where they used similar DFT(D)+U (6 eV) methodology and found  $\angle\text{CO}_2$  to be  $177.1^\circ$  and an adsorption energy of  $-36.4$  kJ/mol.<sup>28</sup> This small change in adsorption energy value is expected as we have not included entropy and enthalpy energy corrections in our calculated adsorption energies.

A Bader charge analysis of the  $(1 \times 1)$  cell (Table III) shows that the oxygen atom O1 of the  $\text{CO}_2$  molecule (bonded to the coordinatively unsaturated surface copper  $\text{Cu}_{\text{CUS}}$ ) gains  $0.03e^-$ , resulting from a small charge transfer from the surface copper atom  $\text{Cu}_{\text{CUS}}$ , which becomes more oxidized after  $\text{CO}_2$  adsorption. This very small charge transfer between the surface and the  $\text{CO}_2$  molecule, as well as small changes in vibrational frequencies (Table III) indicates weak activation of the  $\text{CO}_2$  molecule.

*b. (111):Cu surface.* We calculated the  $\text{CO}_2$  adsorption of numerous input configurations, placing the  $\text{CO}_2$  molecule at different sites on the surface in different orientations, and we found that the  $\text{CO}_2$  molecule binds in two configurations. In the first configuration (config. 1) after optimisation, the top Cu atoms  $\text{Cu}_A$  and  $\text{Cu}_B$  have moved upwards to interact with one of the  $\text{CO}_2$  oxygen atoms O1, as shown in Fig. 10(a). The O1–Cu distances are 1.89 and 1.97 Å for  $\text{Cu}_A$  and  $\text{Cu}_B$ , respectively. The other oxygen atom, O2, of the  $\text{CO}_2$  molecule remained unbound in this configuration. The  $\text{CO}_2$  molecule bends with  $\angle\text{CO}_2 = 125.5^\circ$ , as the carbon atom moved down to interact with a surface oxygen atom,  $\text{O}_{\text{SUF}}$ , in the second layer ( $d_{\text{C}-\text{O}_{\text{SUF}}} = 1.41$  Å). The C–O1 bond length becomes slightly elongated,  $d_{\text{C}-\text{O1}} = 1.34$  Å, while the C–O2 bond is 1.22 Å long, i.e., longer than in the gas phase, which, together with the bending of the  $\text{CO}_2$ , is related to the activation of the molecule.<sup>50</sup> Upon  $\text{CO}_2$  adsorption, the bond distance between the top Cu and O atoms changes from 1.86 Å to 1.83. We

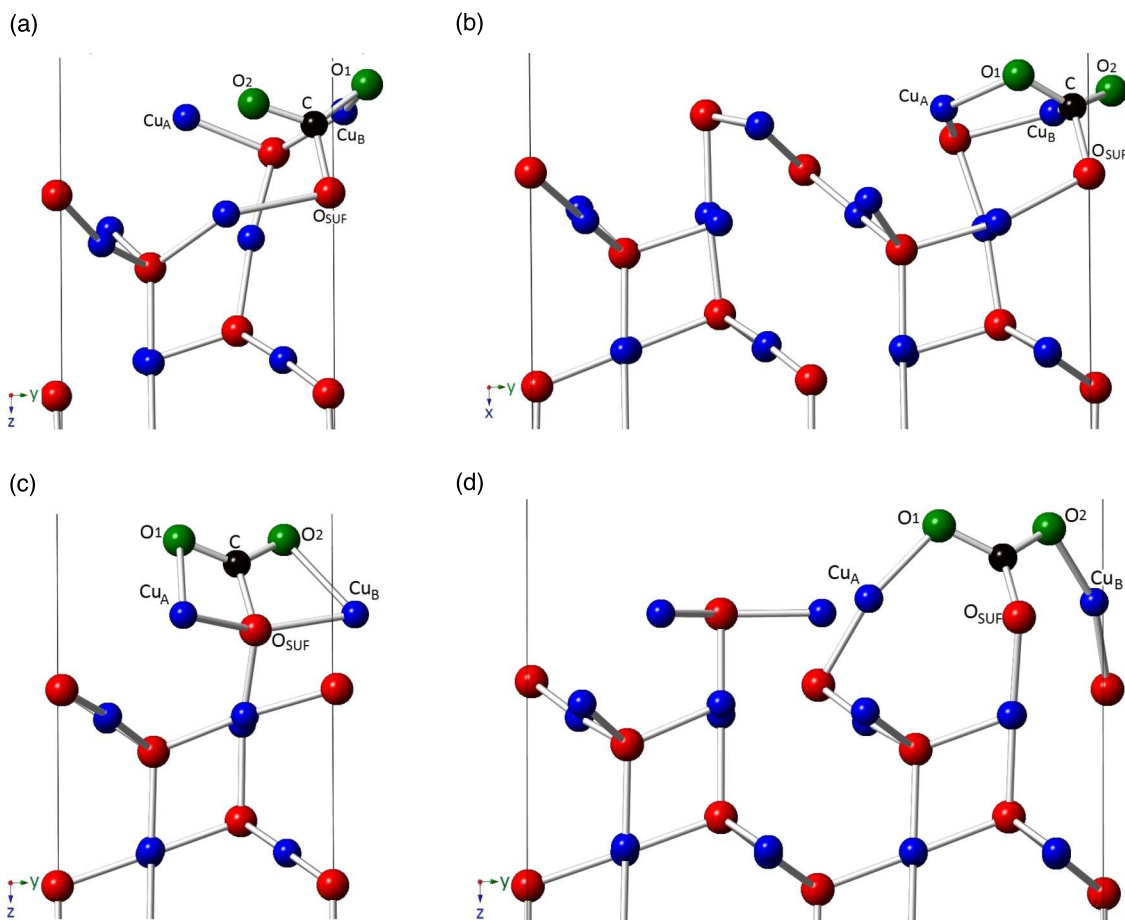


FIG. 10. The  $\text{CO}_2$  molecule adsorbed on the  $\text{Cu}_2\text{O}(111):\text{Cu}$  terminated surface in the (a)  $(1 \times 1)$  cell, (b)  $(1 \times 2)$  supercell in config. 1 and in the (c)  $(1 \times 1)$  cell, (d)  $(1 \times 2)$  supercell in config. 2.

TABLE IV. The adsorption energies and the characteristic parameter values of the CO<sub>2</sub> adsorbed geometry in the (1 × 1) and the (1 × 2) supercell of the Cu<sub>2</sub>O(111):Cu surface in config. 1 and config. 2.

Supercell	E <sub>ads</sub> (kJ/mol)	∠CO <sub>2</sub> (deg)	d <sub>C–O1</sub> (Å)	d <sub>C–O2</sub> (Å)	d <sub>O1–CuA</sub> (Å)	d <sub>O1–CuB</sub> (Å)	d <sub>C–OSUF</sub> (Å)
Config. 1							
(1 × 1)	–117.1	125.5	1.34	1.22	1.89	1.97	1.41
(1 × 2)	–161.5	129.0	1.27	1.27	1.91	1.90	1.42
Config. 2							
(1 × 1)	–97.1	133.2	1.26	1.26	2.14	2.14	1.44
(1 × 2)	–232.6	119.2	1.30	1.30	1.85	1.85	1.32

noted that the surface oxygen atoms, which were connected in a vertical linear manner to Cu and O atoms in the second and third layer, respectively, bend towards the CO<sub>2</sub> molecule with loss of linearity. The adsorption energy calculated in this configuration is –117.1 kJ/mol.

We noted that due to the orientation of the CO<sub>2</sub> molecule, the lateral distance in the x-direction between the CO<sub>2</sub> molecule and its periodic image is 6.04 Å, while in the y-direction, it is only 3.80 Å. Hence, to minimize the effect of the periodic images on the CO<sub>2</sub> adsorption, we carried out calculations on a (1 × 2) supercell. At this lower coverage, CO<sub>2</sub> adsorbs in a slightly different manner, as the top surface Cu atoms (Cu<sub>A</sub> and Cu<sub>B</sub>) interact with both CO<sub>2</sub> oxygen atoms at distances of 2.03 Å and 2.01 Å, respectively (Fig. 10(b)). As a result, the Cu<sub>A</sub> and Cu<sub>B</sub> bond lengths with oxygen atoms in the surface change to 1.91 and 1.90 Å, respectively. Because of the lower coverage of CO<sub>2</sub> molecules on the surface, other surface Cu atoms (further away from the CO<sub>2</sub> molecule) bend inwards to bind to O atoms in the second layer, as shown in Fig. 10(b). As expected, the adsorption energy increases to about –161.5 kJ/mol. Similar to the (1 × 1) cell configuration, the C atom of the CO<sub>2</sub> molecule bends towards a surface oxygen atom O<sub>SUF</sub> in the second layer (d<sub>C–OSUF</sub> = 1.42 Å). The angle of the adsorbed CO<sub>2</sub> molecule is 129.0° and both C–O bond lengths are 1.27 Å. We have given parameters of the CO<sub>2</sub> adsorption geometries in the (1 × 1) and (1 × 2) simulation cells in Table IV.

Bader charge analysis of the (1 × 2) supercell shows charge transfer between the CO<sub>2</sub> molecule and the surface, as both molecular oxygens O1 and O2 gain 0.08e<sup>–</sup> and 0.07e<sup>–</sup> charge densities, respectively. This charge transfer originates mainly from the interacting surface copper atoms Cu<sub>A</sub> and Cu<sub>B</sub>, which become more positively charged after adsorption. The O<sub>SUF</sub> atom bound to the molecule also gains 0.11e<sup>–</sup> charge density (Table V). We also note some charge redistribution

on the Cu<sub>2</sub>O surface as a result of CO<sub>2</sub> adsorption. Bader analysis indicates the CO<sub>2</sub> molecule as a chemisorbed anion on the surface, in agreement with the molecular orbital occupation and bending of the molecule. This activation of the CO<sub>2</sub> molecule is also reflected in terms of changes in the vibrational frequencies of the molecule, as asymmetric (ν<sub>as</sub>) and symmetric (ν<sub>s</sub>) stretching modes change to 1560 and 1200 cm<sup>–1</sup> from their values of 2355 and 1316 cm<sup>–1</sup>, respectively, in the isolated gas phase molecule (Table V).

In a different configuration (config. 2), CO<sub>2</sub> binds to the (111):Cu terminated surface through its C atom to a surface oxygen atom (d<sub>C–OSUF</sub> = 1.44 Å), while both oxygen atoms of the molecule bind to Cu<sub>A</sub> and Cu<sub>B</sub> (d<sub>O–Cu</sub> = 2.14 Å), as shown in Fig. 10(c). The CO<sub>2</sub> molecule again bends to ∠CO<sub>2</sub> = 133.2°, while the Cu–O–Cu angle in the surface is about 145.4°. We found the surface Cu–O bonds to be slightly more stretched with bond distances of 1.98 Å. The adsorption energy at this coverage is –97.1 kJ/mol, which is slightly less than the same coverage in config. 1. Similar to config. 1, we also investigated a lower coverage of CO<sub>2</sub> at the surface in a (1 × 2) supercell (Fig. 10(d)). At this coverage, after CO<sub>2</sub> adsorption, surface rearrangement takes place where copper atoms Cu<sub>A</sub> and Cu<sub>B</sub> break their bonds with the O<sub>SUF</sub> atom to form new bonds to surface oxygen atoms nearby, as well as bind to both CO<sub>2</sub> oxygen atoms (d<sub>O–Cu</sub> = 1.85 Å). The carbon atom binds more strongly to surface atom O<sub>SUF</sub> (d<sub>C–OSUF</sub> = 1.32 Å) as the CO<sub>2</sub> angle changes to ∠CO<sub>2</sub> = 119.0°, and we noted that ∠O<sub>1</sub>–C–O<sub>SUF</sub> and ∠O<sub>2</sub>–C–O<sub>SUF</sub> are ~120.0°. The adsorption energy increases to –232.6 kJ/mol (Table IV). Despite this large adsorption energy, Bader charge comparison (Table V) of the free CO<sub>2</sub> molecule with that in the adsorbed geometry shows that there is very little charge transfer, although large charge redistribution takes place among the surface atoms bonded to the molecule. O<sub>SUF</sub> atom gains 0.23e<sup>–</sup> charge

TABLE V. Vibrational frequencies (cm<sup>–1</sup>) and Bader charges (e<sup>–</sup>) comparison of the atoms in the adsorbed CO<sub>2</sub> molecule and the Cu<sub>2</sub>O(111):Cu surface atoms bonded with the molecule in the (1 × 2) supercell to that of the atoms in the isolated CO<sub>2</sub> molecule and the bare surface in config. 1 and config. 2.

Atoms and vibrational modes	C	O1	O2	Cu <sub>A</sub>	Cu <sub>B</sub>	O <sub>SUF</sub>	ν <sub>as</sub>	ν <sub>s</sub>	ν <sub>b</sub>
After CO <sub>2</sub> adsorption (config. 1)	2.02	–1.12	–1.11	0.54	0.55	–1.03	1560	1200	748
After CO <sub>2</sub> adsorption (config. 2)	2.09	–1.06	–1.07	0.56	0.58	–1.15	1395	1257	858
Isolated CO <sub>2</sub> molecule	2.08	–1.04	–1.04	...	...	...	2355	1316	632
Bare surface	...	...	...	0.41	0.40	–0.92	...	...	...

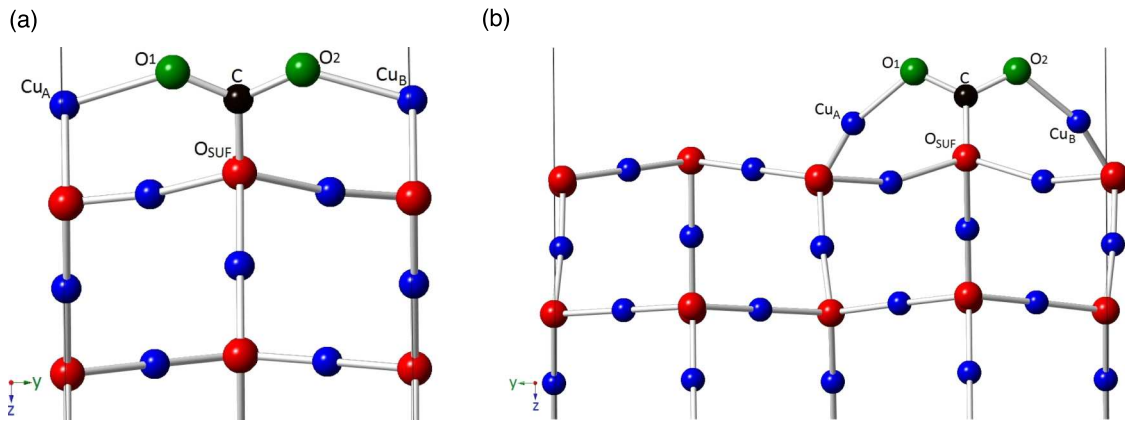


FIG. 11. The  $\text{CO}_2$  molecule adsorbed on the  $\text{Cu}_2\text{O}(110):\text{Cu}$  terminated surface in the (a)  $(1 \times 1)$  cell and in the (b)  $(1 \times 2)$  supercell.

density, while  $\text{Cu}_A$  and  $\text{Cu}_B$  both lose  $0.16e^-$  and  $0.17e^-$  in charge densities, respectively. This charge redistribution together with the change in the surface results in a  $\text{CO}_3^-$  like-species on the  $(111):\text{Cu}$  surface (Fig. 10(d)). Unstable surfaces are often highly reactive, which is exemplified by this behaviour of the  $(111):\text{Cu}$  surface. This strong activation of the  $\text{CO}_2$  molecule is further confirmed by considerable changes in the vibrational modes of the adsorbed  $\text{CO}_2$  molecule, where asymmetric stretch ( $\nu_{as}$ ), symmetric stretch ( $\nu_s$ ), and bending ( $\nu_b$ ) frequencies change to 1395, 1257, and  $858\text{ cm}^{-1}$ , respectively, from their original values of 2355, 1316, and  $632\text{ cm}^{-1}$  in the isolated gas phase molecule.

## 2. $\text{Cu}_2\text{O}(110)$ surface

*a.  $(110):\text{Cu}$ .* For this surface, we first considered a  $(1 \times 1)$  unit cell and tried different initial configurations with several orientations of the  $\text{CO}_2$  molecule, but we found only one configuration in which  $\text{CO}_2$  binds to the surface. Here,  $\text{CO}_2$  binds strongly ( $E_{\text{ads}} = -100\text{ kJ/mol}$ ) in a configuration where the molecule bends to bind with an oxygen atom in the second layer ( $d_{\text{C-OSUF}} = 1.45\text{ \AA}$ ), while its oxygen atoms  $\text{O}_1$  and  $\text{O}_2$  bind to surface atoms,  $\text{Cu}_A$  and  $\text{Cu}_B$ , at  $1.97\text{ \AA}$  (Fig. 11(a)). We noted that the  $\text{CO}_2$  molecule is activated with an angle of  $\angle\text{CO}_2 = 128.0^\circ$ . From Fig. 11(a), we observe that the distance between the  $\text{CO}_2$  molecule and its image in the  $x$ -direction is  $4.3\text{ \AA}$ , while in the  $y$ -direction it is only  $3.78\text{ \AA}$ . We therefore repeated the calculations of all the different configurations in  $(2 \times 1)$  and  $(1 \times 2)$  supercells.

Keeping the same input orientations, we first assessed the effect of a lower  $\text{CO}_2$  coverage by placing one molecule in a  $(2 \times 1)$  supercell and found that  $E_{\text{ads}}$  increased to  $-105.0\text{ kJ/mol}$ , while in the  $(1 \times 2)$  supercell,  $E_{\text{ads}}$  increased to  $-116.7\text{ kJ/mol}$ . This increase in  $E_{\text{ads}}$  was expected because of the small distance between the  $\text{CO}_2$  molecule and its periodic image in the  $y$ -direction in the  $(1 \times 1)$  cell. Because of the significant difference in  $E_{\text{ads}}$  in the  $(1 \times 2)$  supercell compared to the  $(2 \times 1)$  supercell, we have limited our discussion only to the more favourable  $(1 \times 2)$  supercell system. In the  $(1 \times 2)$  supercell, the carbon atom of the molecule binds strongly to the surface oxygen atom ( $d_{\text{C-OSUF}} = 1.42\text{ \AA}$ ), while  $\text{Cu}_A\text{-O}_1$  and  $\text{Cu}_B\text{-O}_2$  bond lengths reduce to  $1.89\text{ \AA}$  (Fig. 11(b)). We have given geometrical parameters of the adsorbed geometry

of the  $(1 \times 1)$  and  $(1 \times 2)$  supercells in Table VI. Bader analysis of the  $(1 \times 2)$  supercell (Table VII) shows charge transfer between the oxygen atoms of  $\text{CO}_2$  and surface copper atoms. Oxygen atoms  $\text{O}_1$  and  $\text{O}_2$  gain  $0.05$  and  $0.06e^-$ , respectively, while both surface copper atoms  $\text{Cu}_A$  and  $\text{Cu}_B$  lose  $0.12e^-$ . There is a very small charge transfer to the carbon atom of the  $\text{CO}_2$  molecule of  $\sim 0.01e^-$ . This amount of charge transfer is consistent with the charge transfer in the  $(111):\text{Cu}$  surface, where the molecule's oxygen gains  $\sim 0.08e^-$  and surface copper atoms lose charge of  $\sim 0.15e^-$ . Here also, frequencies for asymmetric stretch ( $\nu_{as}$ ), symmetric stretch ( $\nu_s$ ), and bending ( $\nu_b$ ) vibrations change to 1639, 1247, and  $808\text{ cm}^{-1}$ , indicating activation of the  $\text{CO}_2$  molecule on the  $(110):\text{Cu}$  surface. In all other configurations considered, the  $\text{CO}_2$  molecule does not bind to the copper oxide surface.

*b.  $(110):\text{Cu-O}$ .* Here again, we carried out calculations on a  $(2 \times 1)$  supercell, exploring different configurations for  $\text{CO}_2$  to bind with the surface. In the first configuration (config. 1), after placing the  $\text{CO}_2$  molecule parallel to the  $\text{Cu-O-Cu}$  linear bond in the top layer, we found that this bond breaks when Cu atoms move up to bind to oxygen atoms of the  $\text{CO}_2$  molecule, while the carbon atom bends down to bind to the oxygen atom of the top surface layer ( $d_{\text{C-OSUF}} = 1.36\text{ \AA}$ ), as shown in Fig. 12(a). One of the  $\text{CO}_2$  oxygen atoms ( $\text{O}_1$ ) binds to one of the nearest Cu atoms ( $\text{Cu}_A$ ) in the top layer with a bond distance  $d_{\text{O}_1\text{-Cu}_A} = 1.84\text{ \AA}$ , while the second oxygen ( $\text{O}_2$ ) binds to another surface copper atom with a bond distance  $d_{\text{O}_2\text{-Cu}_B} = 1.86\text{ \AA}$ , causing the  $\text{Cu-O}$  distances of  $\text{Cu}_A$  and  $\text{Cu}_B$  to their neighbouring surface oxygen atoms to change from  $2.10$  and  $2.18\text{ \AA}$  to  $1.83$  and  $1.84\text{ \AA}$ , respectively. The  $\text{CO}_2$  molecule bends to an angle of  $\angle\text{CO}_2 = 123.6^\circ$  and adsorbs strongly with an adsorption

TABLE VI. The adsorption energies and the characteristic parameter values of the  $\text{CO}_2$  adsorbed geometry in the  $(1 \times 1)$  and the  $(1 \times 2)$  supercell of the  $\text{Cu}_2\text{O}(110):\text{Cu}$  surface.

Supercell	$E_{\text{ads}}$ (kJ/mol)	$\angle\text{CO}_2$ (deg)	$d_{\text{C-O}_1}$ ( $\text{\AA}$ )	$d_{\text{C-O}_2}$ ( $\text{\AA}$ )	$d_{\text{O}_1\text{-Cu}_A}$ ( $\text{\AA}$ )	$d_{\text{O}_1\text{-Cu}_B}$ ( $\text{\AA}$ )	$d_{\text{C-OSUF}}$ ( $\text{\AA}$ )
$(1 \times 1)$	-100.4	128.0	1.26	1.26	1.97	1.97	1.45
$(1 \times 2)$	-116.7	126.2	1.26	1.26	1.89	1.89	1.42



TABLE VII. Vibrational frequencies ( $\text{cm}^{-1}$ ) and Bader charges ( $e^-$ ) comparison of the atoms in the adsorbed  $\text{CO}_2$  molecule and the  $\text{Cu}_2\text{O}(110):\text{Cu}$  surface atoms bonded with the molecule to that of in the isolated  $\text{CO}_2$  molecule and the bare surface in the  $(1 \times 2)$  supercell.

Atoms and vibrational modes	C	O1	O2	$\text{Cu}_A$	$\text{Cu}_B$	$\text{O}_{\text{SUF}}$	$\nu_{\text{as}}$	$\nu_{\text{s}}$	$\nu_{\text{b}}$
After $\text{CO}_2$ adsorption	2.07	-1.09	-1.10	0.56	0.56	-1.04	1639	1247	808
Isolated $\text{CO}_2$ molecule	2.08	-1.04	-1.04	...	...	...	2355	1316	632
Bare surface	...	...	...	0.44	0.44	-0.95	...	...	...

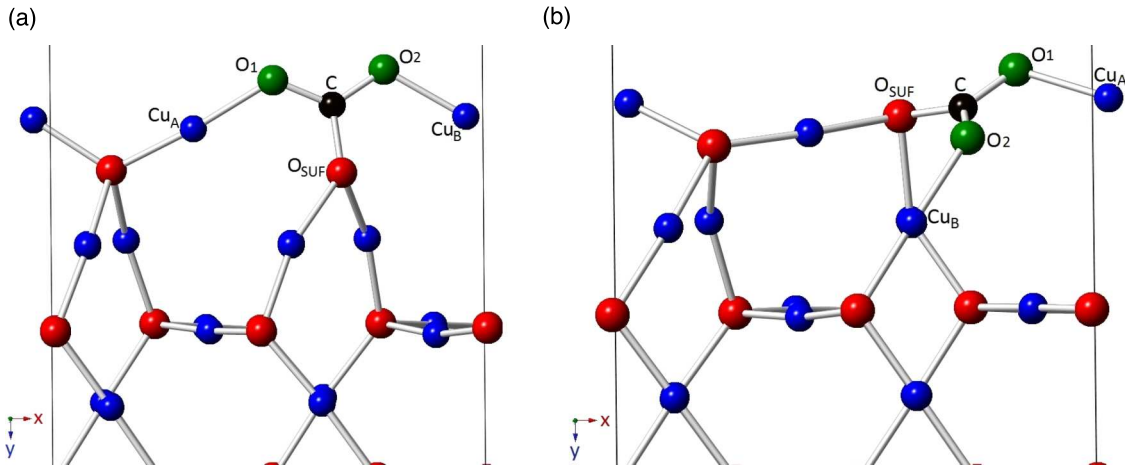


FIG. 12. The  $\text{CO}_2$  molecule adsorbed on the  $\text{Cu}_2\text{O}(110):\text{Cu}-\text{O}$  terminated surface in the  $(2 \times 1)$  cell in (a) config. 1 and (b) config. 2.

energy  $E_{\text{ads}} = -138.1$  kJ/mol. In this configuration, the C–O bond length is  $1.27 \text{ \AA}$ , which is slightly longer than the normal bond length in a  $\text{CO}_2$  molecule. The adsorption energy and geometrical parameters of the system are given in Table VIII. Bader charge analysis (Table IX) reveals that the O1 and O2 oxygen atoms of the  $\text{CO}_2$  molecule gain  $0.13$  and  $0.10e^-$  in charge density, respectively. Meanwhile, the surface copper atoms,  $\text{Cu}_A$  and  $\text{Cu}_B$ , which are bound to the O1 and O2 lose a charge density of  $0.49$  and  $0.39e^-$ , respectively, while the surface oxygen atom ( $\text{O}_{\text{SUF}}$ ) bound to the carbon atom of the  $\text{CO}_2$  molecule gains  $0.14e^-$ . Hence, upon  $\text{CO}_2$  adsorption, a large charge redistribution occurs at the surface. This strong adsorption and activation of the  $\text{CO}_2$  molecule are reflected in changes in the vibrational frequencies, as listed in Table IX.

In the second configuration (config. 2) (Fig. 12(b)), the carbon atom binds to the  $\text{O}_{\text{SUF}}$  atom ( $d_{\text{C}-\text{O}_{\text{SUF}}} = 1.35 \text{ \AA}$ ) and O1 binds to  $\text{Cu}_A$  ( $d_{\text{O1}-\text{Cu}_A} = 1.85 \text{ \AA}$ ) in the top layer. The  $\text{CO}_2$  molecule bends so that O2 binds with  $\text{Cu}_B$  of the second

layer ( $d_{\text{O2}-\text{Cu}_B} = 1.86 \text{ \AA}$ ), as shown in Fig. 12(b). In this configuration, we found that  $\text{CO}_2$  binds more strongly with an adsorption energy of about  $-170.0$  kJ/mol.  $\text{CO}_2$  bends to an angle of  $\angle \text{CO}_2 = 122.7^\circ$  which indicates stronger activation (Table VIII). Oxygen–carbon bond lengths, i.e.,  $d_{\text{C}-\text{O1}}$  and  $d_{\text{C}-\text{O2}}$ , are found to be  $1.27 \text{ \AA}$  and  $1.30 \text{ \AA}$ , respectively. After  $\text{CO}_2$  adsorption, the Cu–O bonds in the top of the surface change from  $2.10 \text{ \AA}$  and  $2.18 \text{ \AA}$  to  $1.86 \text{ \AA}$  and  $1.82 \text{ \AA}$  for  $\text{Cu}_A$  and  $\text{Cu}_B$ , respectively. Bader charge analysis (Table IX) shows that the oxygen atoms O1 and O2 of the  $\text{CO}_2$  molecule gain  $-0.13$  and  $-0.08e^-$ , respectively, while the change in the carbon atom charge is negligible. The surface copper atom  $\text{Cu}_A$  bonded to one of the oxygen atoms of the  $\text{CO}_2$  molecule becomes more positively charged with a loss of  $0.26e^-$ , while the surface oxygen atom  $\text{O}_{\text{SUF}}$  gains  $0.23e^-$ . Charge transfer to  $\text{Cu}_B$  is negligible. This charge transfer, the adsorption energy, geometry changes together with large changes in vibrational frequencies (Table IX) indicates activation of the  $\text{CO}_2$  molecule.

### 3. $\text{Cu}_2\text{O}(001)$ surface

*a. (001):Cu.* The  $(1 \times 1)$  cell ( $a = 4.27 \text{ \AA}$ ,  $b = 4.27 \text{ \AA}$ ) is too small to study adsorption of the isolated molecule, as we discovered earlier that the interaction between neighbouring  $\text{CO}_2$  molecules affects the geometry and adsorption energies. Hence, we carried out calculations on the  $(2 \times 2)$  supercell to minimize the effect of interactions between periodic images. Similar to the other surfaces, we studied different sites at the surface for possible  $\text{CO}_2$  adsorption. In the first adsorption configuration (config. 1), oxygens O1 and O2 of the molecule bind to the nearest topmost copper atoms

TABLE VIII. The adsorption energies and the characteristic parameter values of the  $\text{CO}_2$  adsorbed geometry in the  $(2 \times 1)$  supercell of the  $\text{Cu}_2\text{O}(110):\text{Cu}-\text{O}$  surface in config. 1 and config. 2.

Supercell	$E_{\text{ads}}$ (kJ/mol)	$\angle \text{CO}_2$ (deg)	$d_{\text{C}-\text{O1}}$ ( $\text{\AA}$ )	$d_{\text{C}-\text{O2}}$ ( $\text{\AA}$ )	$d_{\text{O1}-\text{Cu}_A}$ ( $\text{\AA}$ )	$d_{\text{O2}-\text{Cu}_B}$ ( $\text{\AA}$ )	$d_{\text{C}-\text{O}_{\text{SUF}}}$ ( $\text{\AA}$ )
Config. 1							
$(2 \times 1)$	-138.1	123.6	1.27	1.27	1.84	1.86	1.36
Config. 2							
$(2 \times 1)$	-169.9	122.7	1.27	1.30	1.85	1.86	1.35

TABLE IX. Vibrational frequencies ( $\text{cm}^{-1}$ ) and Bader charges ( $e^-$ ) comparison of the atoms in the adsorbed  $\text{CO}_2$  molecule and the  $\text{Cu}_2\text{O}(110):\text{Cu}-\text{O}$  surface atoms bonded with the molecule to that of in the isolated  $\text{CO}_2$  molecule and the bare surface in config. 1 and config. 2 of  $(2 \times 1)$  supercell.

Atoms and vibrational modes	C	O1	O2	Cu <sub>A</sub>	Cu <sub>B</sub>	O <sub>SUF</sub>	$\nu_{\text{as}}$	$\nu_{\text{s}}$	$\nu_{\text{b}}$
After $\text{CO}_2$ adsorption (config. 1)	2.07	-1.14	-1.17	0.91	0.81	-1.03	1580	1291	869
After $\text{CO}_2$ adsorption (config. 2)	2.07	-1.17	-1.12	0.53	0.69	-1.12	1508	1250	851
Isolated $\text{CO}_2$ molecule	2.08	-1.04	-1.04	...	...	...	2355	1316	632
Bare surface	...	...	...	0.42	0.42	-0.89	...	...	...

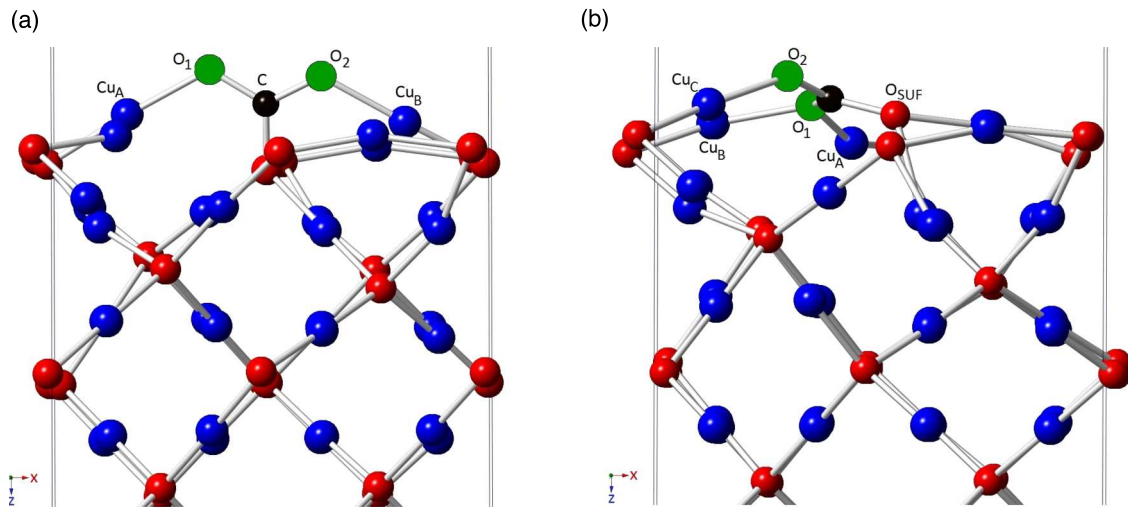


FIG. 13. The  $\text{CO}_2$  molecule adsorbed on the  $\text{Cu}_2\text{O}(001):\text{Cu}$  terminated surface in the  $(2 \times 2)$  cell in (a) config. 1 and (b) config. 2.

$\text{Cu}_A$  and  $\text{Cu}_B$  with bond distances of 1.85 and 1.87 Å, respectively (Fig. 13(a)). The  $\text{CO}_2$  molecule bends to an angle of  $121.5^\circ$  as the carbon atom moves down to bind with the nearest available oxygen atom ( $\text{O}_{\text{SUF}}$ ) of the top layer with a bond length  $d_{\text{C}-\text{O}_{\text{SUF}}}$  of 1.35 Å. Upon  $\text{CO}_2$  adsorption, the bond between  $\text{Cu}_B$  and  $\text{O}_{\text{SUF}}$  is broken, as shown in Fig. 8(a). The adsorption energy,  $E_{\text{ads}}$ , calculated for this configuration is  $-138$  kJ/mol. Carbon-oxygen bond lengths in the  $\text{CO}_2$  molecule are found to be 1.29 and 1.28 Å for O1 and O2, respectively. Copper-oxygen bond lengths in the surface for  $\text{Cu}_A$  and  $\text{Cu}_B$  change from 1.88 to 1.84 Å and 1.86 Å, respectively (Table X). Bader charge analysis (Table XI) shows significant charge transfer between the  $\text{CO}_2$  molecule and the surface atoms. After  $\text{CO}_2$  adsorption, both O1 and O2 oxygens of the  $\text{CO}_2$  molecule lose charge density of  $0.24e^-$  and  $0.22e^-$ , respectively, while surface copper atoms  $\text{Cu}_A$  and  $\text{Cu}_B$  which bind to these two oxygen atoms lose charge density of 0.12 and  $0.10e^-$ , respectively. However, the carbon

atom gains  $0.56e^-$  after binding to surface oxygen atom  $\text{O}_{\text{SUF}}$ , which loses  $0.12e^-$ . Hence, charge transfer has occurred to the  $\text{CO}_2$  molecule from nearby surface atoms. As shown in Table XI, we note considerable changes in the frequencies of the different vibrational modes ( $\nu_{\text{as}} = 1509$ ,  $\nu_{\text{s}} = 1281$ , and  $\nu_{\text{b}} = 869 \text{ cm}^{-1}$ ) of the activated  $\text{CO}_2$  molecule on this surface. In another configuration (config. 2) the  $\text{CO}_2$  molecule remains almost parallel to the surface, as shown in Fig. 13(b). The carbon atom binds to a top oxygen atom ( $\text{O}_{\text{SUF}}$ ) ( $d_{\text{C}-\text{O}_{\text{SUF}}} = 1.32$  Å), while one oxygen (O1) of the  $\text{CO}_2$  molecule binds to surface copper atoms  $\text{Cu}_A$  and  $\text{Cu}_B$ , with bond lengths 1.95 and 1.91 Å, respectively. The second oxygen atom (O2) of the molecule binds to another surface copper atom,  $\text{Cu}_C$  with a bond length of 1.91 Å. In the adsorbed  $\text{CO}_2$  molecule we find O-C bond lengths of 1.32 and 1.27 Å for oxygen atoms O1 and O2, respectively, and the  $\text{CO}_2$  angle is  $\angle\text{CO}_2 = 121.7^\circ$ . The adsorption energy in this configuration is  $-98.7$  kJ/mol, which is almost 40 kJ/mol less than in the

TABLE X. The adsorption energies and the characteristic parameter values of the  $\text{CO}_2$  adsorbed geometry in the  $(2 \times 2)$  supercell of  $\text{Cu}_2\text{O}(001):\text{Cu}$  surface in config. 1 and config. 2.

Supercell	$E_{\text{ads}}$ (kJ/mol)	$\angle\text{CO}_2$ (deg)	$d_{\text{C}-\text{O1}}$ (Å)	$d_{\text{C}-\text{O2}}$ (Å)	$d_{\text{O1}-\text{CuA}}$ (Å)	$d_{\text{O1}-\text{CuB}}$ (Å)	$d_{\text{O2}-\text{CuB}}$ (Å)	$d_{\text{O2}-\text{CuC}}$ (Å)	$d_{\text{C}-\text{OSUF}}$ (Å)
Config. 1									
$(2 \times 2)$	-138.1	121.5	1.29	1.28	1.85	...	1.87	...	1.35
Config. 2									
$(2 \times 2)$	-98.7	121.7	1.32	1.27	1.95	1.91	...	1.91	1.32

TABLE XI. Vibrational frequencies ( $\text{cm}^{-1}$ ) and Bader charges ( $e^-$ ) comparison of the atoms in the adsorbed  $\text{CO}_2$  molecule and  $\text{Cu}_2\text{O}(001):\text{Cu}$  surface atoms bonded with the molecule to that of in the isolated  $\text{CO}_2$  molecule and the bare surface in config. 1 and config. 2 of  $(2 \times 2)$  supercell.

Atoms and vibrational modes	C	O1	O2	Cu <sub>A</sub>	Cu <sub>B</sub>	Cu <sub>C</sub>	O <sub>SUF</sub>	$v_{\text{as}}$	$v_{\text{s}}$	$v_{\text{b}}$
After $\text{CO}_2$ adsorption (config. 1)	1.52	-0.80	-0.82	0.46	0.44	...	-0.77	1509	1281	869
After $\text{CO}_2$ adsorption (config. 2)	1.86	-0.96	-1.11	0.59	0.61	0.65	-0.93	1461	1242	875
Isolated $\text{CO}_2$ molecule	2.08	-1.04	-1.04	...	...	...	...	2355	1316	632
Bare surface	...	...	...	0.34	0.34	0.51	-0.89	...	...	...

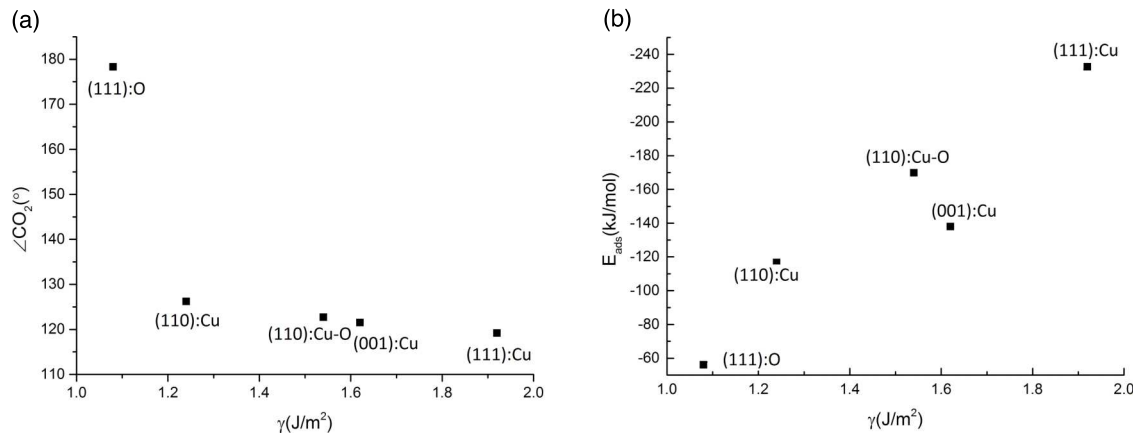


FIG. 14. The variation of  $\text{CO}_2$  activation ( $\angle \text{OCO}$ ) (a) and adsorption energy ( $E_{\text{ads}}$ ) (b) with surface energies of different surfaces. For the sake of simplicity we have plotted only lowest coverage values of only those configurations that show strongest binding with  $\text{CO}_2$ .

first configuration (Table X). The Bader charge analysis shows charge redistribution, with oxygen O1 losing  $0.08e^-$  charge density, while the Cu<sub>A</sub> and Cu<sub>B</sub> atoms also lose  $0.25e^-$  and  $0.27e^-$ , respectively. Oxygen atom O2 gains  $0.07e^-$  charge density after binding to surface copper atom Cu<sub>C</sub>, which loses  $0.14e^-$ . Charge transfer also occurs between surface oxygen atom, O<sub>SUF</sub> and the C atom which gains  $0.22e^-$ , while O<sub>SUF</sub> gains  $0.04e^-$  (Table XI). Here again, we note considerable changes in the vibrational frequencies of the adsorbed  $\text{CO}_2$  molecule, as shown in Table XI.

### C. $\text{CO}_2$ adsorption trends in copper oxides

We noted that the activation of the  $\text{CO}_2$  molecule is related to the adsorption energy, as shown in Fig. 14(a), where we considered the molecule's angle as a measure of its activation.<sup>50</sup> Furthermore, the adsorption energy,  $E_{\text{ads}}$ , depends almost linearly on the surface stability (Fig. 14(b)). The most stable (111):O surface shows weak adsorption (approximately  $-56$  kJ/mol) and the  $\text{CO}_2$  molecule remains linear, while the least stable (111):Cu surface shows the strongest binding ( $E_{\text{ads}} = -233$  kJ/mol) with the  $\text{CO}_2$  molecule bent to  $119.2^\circ$ . The second most stable surface, (110):Cu, shows an adsorption energy of approximately  $-117$  kJ/mol, while the (001):Cu surface, binds the  $\text{CO}_2$  molecule with the release of  $\sim 138$  kJ/mol, with the  $\text{CO}_2$  molecule bending to  $126.2$  and  $121.5^\circ$ , respectively. This trend is similar to that found in  $\text{CO}_2$  adsorption on CuO surfaces, where the most stable surface, (111), shows weak binding of the  $\text{CO}_2$  molecule compared with other low index surfaces, which cause significant  $\text{CO}_2$  activation.<sup>11</sup>

## IV. SUMMARY AND CONCLUSIONS

Using DFT+U methodology, we have studied the reconstructions of the (111), (110), and (001) surfaces and proposed different non-polar terminations. We further analysed the structural geometries, energetics, and electronic properties for the process of carbon dioxide adsorption to different stoichiometric  $\text{Cu}_2\text{O}$  surfaces, at different coverages. While the  $\text{CO}_2$  adsorption to stoichiometric  $\text{Cu}_2\text{O}(111):\text{O}$  is weak, causing no significant changes to the geometry or electronic structure of the adsorbate,  $\text{CO}_2$  adsorption to all other surfaces is energetically favourable. The (110):Cu surface, which is only less stable by  $\sim 0.16$  J/m<sup>2</sup> compared to the most stable (111):O surface, shows adsorption energies up to approximately  $-117$  kJ/mol, while the third most stable (110):Cu-O surface exhibits strong chemisorption of the  $\text{CO}_2$  molecule, releasing  $\sim 170$  kJ/mol. We found that  $\text{CO}_2$  coverage affects the adsorption energy as  $E_{\text{ads}}$  increases for all surfaces at lower coverage, where  $\text{CO}_2$  is found to be chemisorbed as the  $\text{CO}_2^-$  anion. The  $\text{Cu}_2\text{O}(111)$  surface with Cu termination is found to be the least stable surface and a detailed structural and Bader charge analysis shows that the  $\text{CO}_2$  molecule affects the surface geometry, rearranging itself to resemble a  $[\text{CO}_3]^-$  species on the surface.

Activation of carbon dioxide is the most important step in its conversion into valuable chemicals and large structural transformations and significant charge transfer between different surfaces and the  $\text{CO}_2$  molecule demonstrate that  $\text{Cu}_2\text{O}$  is capable of activating  $\text{CO}_2$ . For all the bent  $\text{CO}_2$  configurations, we note a significant red-shift on the C-O symmetric ( $v_{\text{s}}$ ) and asymmetric ( $v_{\text{as}}$ ) stretching modes relative to the linear gas phase molecule, indicating that the



CO<sub>2</sub> molecule is considerably activated. It is worth noting, however, that our calculations are valid only at 0 K and only stoichiometric surfaces were considered in the present study. Nevertheless, the results presented in this paper provide fundamental mechanistic insights into CO<sub>2</sub> activation on stoichiometric (111), (110), and (001) surfaces, which will still be relevant to our general understanding of CO<sub>2</sub> adsorption by Cu<sub>2</sub>O, as the different surfaces studied here include a wide variety of the kind of surface sites, that can be expected to occur on experimental surfaces.

## SUPPLEMENTARY MATERIAL

The reconstructed unrelaxed surface structures of (111):Cu, (110):Cu, (110):CuO–O, and (001):Cu are given as Figs. S1–S4 in the [supplementary material](#), respectively.

## ACKNOWLEDGMENTS

This work was carried out as part of the Engineering and Physical Sciences Research Council (EPSRC) “4CU” programme grant, aimed at sustainable conversion of carbon dioxide into fuels, led by The University of Sheffield and carried out in collaboration with University College London, University of Manchester, and Queens University Belfast. The authors acknowledge the EPSRC for supporting this work financially (Grant Nos. EP/K001329/1 and EP/K035355/1). Via our membership of the UK’s HEC Materials Chemistry Consortium, which is funded by EPSRC (Grant No. EP/L000202), this work used the ARCHER UK National Supercomputing Service (<http://www.archer.ac.uk>). The authors also acknowledge the use of the IRIDIS High Performance Computing Facility, and associated support services at the University of Southampton, in the completion of this work. N.H.d.L. thanks the Royal Society for an Industry Fellowship.

<sup>1</sup>Y. Hori, in *Modern Aspects of Electrochemistry*, edited by C. Vayenas, R. White, and M. Gamboa-Aldeco (Springer, New York, 2008), Vol. 42, Chap. 3, pp. 89–189.

<sup>2</sup>M. Gattrell, N. Gupta, and A. Co, *J. Electroanal. Chem.* **594**, 1 (2006).

<sup>3</sup>J. Szanyi and D. W. Goodman, *Catal. Lett.* **10**, 383 (1991).

<sup>4</sup>T. Matsumoto, R. A. Bennett, P. Stone, T. Yamada, K. Domen, and M. Bowker, *Surf. Sci.* **471**, 225 (2001).

<sup>5</sup>S. Y. Lee, N. Mettlach, N. Nguyen, Y. M. Sun, and J. M. White, *Appl. Surf. Sci.* **206**, 102 (2003).

<sup>6</sup>A. K. Mishra and N. H. de Leeuw, “Mechanistic insights into the Cu(I) oxide-catalyzed conversion of CO<sub>2</sub> to fuels and chemicals: A DFT approach,” *J. CO<sub>2</sub> Util.* (in press).

<sup>7</sup>M. Le, M. Ren, Z. Zhang, P. T. Sprunger, R. L. Kurtz, and J. C. Flake, *J. Electrochem. Soc.* **158**, E45 (2011).

<sup>8</sup>G. Ghadimkhani, N. R. de Tacconi, W. Chanmanee, C. Janaky, and K. Rajeshwar, *Chem. Commun.* **49**, 1297 (2013).

<sup>9</sup>C. Wang, L. Yin, L. Zhang, D. Xiang, and R. Gao, *Sensors (Basel)* **10**, 2088 (2010).

<sup>10</sup>O. Lupan, V. Cretu, V. Postica, N. Ababii, O. Polonskyi, V. Kaidas, F. Schütt, Y. K. Mishra, E. Monaico, I. Tiginyanu, V. Sontea, T. Strunskus, F. Faupel, and R. Adelung, *Sens. Actuators, B* **224**, 434 (2016).

<sup>11</sup>V. Cretu, V. Postica, A. K. Mishra, M. Hoppe, I. Tiginyanu, Y. K. Mishra, L. Chow, N. H. de Leeuw, R. Adelung, and O. Lupan, *J. Mater. Chem.* **4**, 6527 (2016).

<sup>12</sup>A. K. Mishra, A. Roldan, and N. H. de Leeuw, *J. Phys. Chem. C* **120**, 2198 (2016).

<sup>13</sup>Z. K. Zheng, B. B. Huang, Z. Y. Wang, M. Guo, X. Y. Qin, X. Y. Zhang, P. Wang, and Y. Dai, *J. Phys. Chem. C* **113**, 14448 (2009).

<sup>14</sup>B. Z. Sun, W. K. Chen, and Y. J. Xu, *J. Chem. Phys.* **133**, 154502 (2010).

<sup>15</sup>C. Li, F. Wang, S. F. Li, Q. Sun, and Y. Jia, *Phys. Lett. A* **374**, 2994 (2010).

<sup>16</sup>B. Z. Sun, W. K. Chen, X. Wang, Y. Li, and C. H. Lu, *Chin. J. Inorg. Chem.* **24**, 340 (2008).

<sup>17</sup>W.-K. Chen, B.-Z. Sun, X. Wang, and C.-H. Lu, *J. Theor. Comput. Chem.* **7**, 263 (2008).

<sup>18</sup>H. Wu, N. Zhang, Z. Cao, H. Wang, and S. Hong, *Int. J. Quantum Chem.* **112**, 2532 (2012).

<sup>19</sup>H. Wu, N. Zhang, H. Wang, and S. Hong, *Chem. Phys. Lett.* **568–569**, 84 (2013).

<sup>20</sup>Y. Tan, X. Xue, Q. Peng, H. Zhao, T. Wang, and Y. Li, *Nano Lett.* **7**, 3723 (2007).

<sup>21</sup>M. Pang and H. C. Zeng, *Langmuir* **26**, 5963 (2010).

<sup>22</sup>Y. Sui, W. Fu, H. Yang, Y. Zeng, Y. Zhang, Q. Zhao, Y. Li, X. Zhou, Y. Leng, M. Li, and G. Zou, *Cryst. Growth Des.* **10**, 99 (2009).

<sup>23</sup>X. Zhao, Z. Bao, C. Sun, and D. Xue, *J. Cryst. Growth* **311**, 711 (2009).

<sup>24</sup>S. Sun, F. Zhou, L. Wang, X. Song, and Z. Yang, *Cryst. Growth Des.* **10**, 541 (2009).

<sup>25</sup>S. Sun, C. Kong, S. Yang, L. Wang, X. Song, B. Ding, and Z. Yang, *CrystEngComm* **13**, 2217 (2011).

<sup>26</sup>S. Sun, X. Song, Y. Sun, D. Deng, and Z. Yang, *Catal. Sci. Technol.* **2**, 925 (2012).

<sup>27</sup>E. L. Uzunova, N. Seriani, and H. Mikosch, *Phys. Chem. Phys.* **17**, 11088 (2015).

<sup>28</sup>L. I. Bendavid and E. A. Carter, *J. Phys. Chem. C* **117**, 26048 (2013).

<sup>29</sup>L. Wang, T. Maxisch, and G. Ceder, *Phys. Rev. B* **73**, 174112 (2006).

<sup>30</sup>L. Y. Isseroff and E. A. Carter, *Phys. Rev. B* **85**, 235142 (2012).

<sup>31</sup>M. Nolan and S. D. Elliott, *Phys. Chem. Chem. Phys.* **8**, 5350 (2006).

<sup>32</sup>D. O. Scanlon, B. J. Morgan, and G. W. Watson, *J. Chem. Phys.* **131**, 124703 (2009).

<sup>33</sup>C. E. Ekuma, V. I. Anisimov, J. Moreno, and M. Jarrell, *Eur. Phys. J. B* **87**, 23 (2014).

<sup>34</sup>G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).

<sup>35</sup>G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).

<sup>36</sup>G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).

<sup>37</sup>G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).

<sup>38</sup>S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, *Phys. Rev. B* **57**, 1505 (1998).

<sup>39</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

<sup>40</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **78**, 1396 (1997).

<sup>41</sup>G. W. Watson, E. T. Kelsey, N. H. de Leeuw, J. D. Harris, and S. C. Parker, *J. Chem. Soc., Faraday Trans.* **92**, 433 (1996).

<sup>42</sup>P. W. Tasker, *J. Phys. C: Solid State Phys.* **12**, 4977 (1979).

<sup>43</sup>H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).

<sup>44</sup>G. Wulff, *Z. Kristallogr.* **34**, 449 (1901).

<sup>45</sup>S. Grimme, *J. Comput. Chem.* **27**, 1787 (2006).

<sup>46</sup>A. Werner and H. D. Hochheimer, *Phys. Rev. B* **25**, 5929 (1982).

<sup>47</sup>A. Soon, M. Todorova, B. Delley, and C. Stampfl, *Phys. Rev. B* **75**, 125420 (2007).

<sup>48</sup>J. A. Assimos and D. Trivich, *Phys. Status Solidi A* **26**, 477 (1974).

<sup>49</sup>B. Z. Sun, W. K. Chen, X. Wang, and C. H. Lu, *Appl. Surf. Sci.* **253**, 7501 (2007).

<sup>50</sup>H. J. Freund and M. W. Roberts, *Surf. Sci. Rep.* **25**, 225 (1996).